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2 Two Scientific Communities Striving for a Common Cause: innovations in carbon cycle science

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18 Abstract

19 Where does the carbon released by burning fossil fuels go? Currently, ocean and land systems 20 remove about half of the CO₂ emitted by human activities; the remainder stays in the 21 atmosphere. These removal processes are sensitive to feedbacks in the energy, carbon, and water 22 cycles that will change in the future. Observing how much carbon is taken up on land through 23 photosynthesis is complicated because carbon is simultaneously respired by plants, animals, and 24 microbes. Global observations from satellites and air samples suggest that natural ecosystems take up about as much CO₂ as they emit. To match the data, our land models generate imaginary 25 26 Earths where carbon uptake and respiration are roughly balanced, but the absolute quantities of 27 carbon being exchanged vary widely. Getting the magnitude of the flux is essential to make sure 28 our models are capturing the right pattern for the right reasons.

29 Combining two cutting edge tools, carbonyl sulfide (OCS) and solar-induced fluorescence (SIF), 30 will help develop an independent answer of how much carbon is being taken up by global 31 ecosystems. Photosynthesis requires CO₂, light, and water. OCS provides a spatially and temporally-integrated picture of the 'front door' of photosynthesis, proportional to CO₂ uptake 32 33 and water loss through plant stomata. SIF provides a high-resolution snapshot of the 'side door', 34 scaling with the light captured by leaves. These two independent pieces of information help us 35 understand plant water and carbon exchange. A coordinated effort to generate SIF and OCS data 36 through satellite, airborne, and ground observations will improve our process-based models to 37 predict how these cycles will change in the future.

39 Introduction

40 Photosynthesis is the largest flux of the global carbon cycle, and yet the amount of carbon being 41 fixed by plants is highly uncertain. At scales larger than a single leaf, measuring CO₂ uptake is 42 complicated by the release of CO_2 via respiration at the same time and place. We can observe 43 the net effect of photosynthesis and respiration by measuring CO₂ alone, via satellites like 44 NASA's OCS-2 and OCO-3 or the long record from the NOAA Cooperative Air Sampling 45 Network. Two approaches have emerged capable of isolating the carbon uptake from 46 photosynthesis at large spatial scales: measurements of atmospheric carbonyl sulfide (OCS) and 47 solar-induced fluorescence (SIF). The strength of both SIF and OCS is the ability to scale 48 measurements up to vast regions. However, perhaps because these methods rely on different 49 parts of the photosynthetic machinery, the communities developing these techniques have had 50 limited overlap.

51 Low daytime concentrations of atmospheric OCS indicate that nearby plants are consuming CO₂. 52 The first step for plants to remove CO_2 from the atmosphere is the physical movement of the gas 53 through stomata, tiny openings on leaves, usually at the cost of losing water. Plants open and 54 close their stomata to regulate carbon and water exchange. While we have a good understanding 55 of the chemistry behind photosynthesis, we still have a limited understanding of the mechanisms 56 behind this stomatal functioning. OCS has a similar structure to CO₂ and interacts with the same 57 enzymes, independent of light conditions. Most OCS is made in the oceans or emitted from 58 certain industries like rayon manufacturing. Most OCS is consumed in plant leaves after 59 diffusing through stomata. Observing the lowered concentrations of OCS over vegetated areas 60 tells us how wide the 'front door' of photosynthesis is open (Whelan et al. 2018).

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61 When leaves absorb light, a small fraction is reemitted at a longer wavelength through 62 fluorescence. SIF is a measure of new photons emitted from the excited state of chlorophyll-A, a chief player in photosynthesis, after absorption of solar light, thereby providing insight into the 63 64 light reactions of photosynthesis. Some SIF photons are produced in parts of the spectrum where 65 solar light is absent. Using high-resolution spectrometers, the SIF photons can be distinguished 66 from reflected sunlight. In practice, the magnitude of SIF is proportional to the amount of light 67 intercepted by light-dependent machinery, or the 'side door' of photosynthesis. Measuring the amount of light re-emitted by leaves gives us an idea of how much light is getting through the 68 69 door and ultimately used to power photosynthesis (Porcar-Castell et al. 2014). 70 Both SIF and OCS tools together cover spatial and temporal domains that elude other measures 71 of photosynthesis. We can already quantify carbon uptake instantaneously on the individual leaf 72 scale with small leaf chambers attached to water and CO_2 gas analyzers. With eddy covariance 73 flux towers (Baldocchi et al., 2019), we can estimate photosynthesis on the half hourly and 1 km² 74 scales by observing the net CO_2 exchange and subtracting out modeled respiration from 75 observations at nighttime or periods when photosynthesis is small or absent. SIF data from 76 satellites expands our purview to instant snapshots of multiple km², as often as the satellite can sample. On the ground and from aircraft, SIF spectrometers can give us canopy level estimates 77 78 that relate directly to the leaf biochemistry, rather than involving the uncertainty of respiration 79 estimates. Where SIF data are sparse because of thick clouds or limited satellite overpasses, OCS observations can represent the integrated signal of carbon uptake over a much larger landscape. 80 81 Leveraging the power of both a light-based and a gas-based tracer fills in important gaps in our 82 knowledge of how much carbon our terrestrial ecosystems can pull out of the air.

The uncertainties of SIF and OCS measurements are eclipsed by our remaining process-level questions about photosynthesis and respiration on the continental to global scales. As with any observational approach, there are systematic uncertainties in either. Luckily, OCS and SIF are used to estimate the same parameters while being affected by separate sources of uncertainty. By using both OCS and SIF to constrain our estimates of carbon fluxes, we will reduce our total uncertainties.

90 Most photons intercepted by chlorophyll go to either photochemistry (for food) or

91 nonphotochemical quenching (for protection), with only 1-2% re-emitted as SIF. Subtle

92 variations in this efficiency, termed fluorescence yield, contain detailed information about leaf-

93 level biochemistry (Weis and Berry 1987). Reducing the signal further, some of those newly

94 emitted photons are intercepted by other leaves in the canopy. This can actually be turned to our

95 advantage: the variations in SIF measured by canopy scanning spectrometers give us information

96 about plant canopy structure, providing additional information about whole-plant productivity

97 that appears to be mostly independent from concerns of fluorescence yield or light absorption

98 (Zeng et al. 2019). SIF holds the promise of not only providing a new boon of information about

99 leaf-level biochemistry, but also an entirely new way to study canopy structure and within-

100 canopy light absorption

101 Remotely sensing SIF still has challenges; however, we can take solace in the fact that none of 102 the satellite missions from which SIF is currently derived were specifically designed for 103 dedicated SIF measurements. Rather, satellite-based SIF observations was were enabled in a 104 fortuitous manner as SIF emissions share a similar spectral range to that needed for cloud and trace gas detection. For SIF, this has led to issues such as low signal-to-noise and coarse satellite
pixels, which have complicated scientific interpretation. Fortunately, new technologies and
observing strategies are likely to overcome many of these challenges.

Since OCS is an atmospheric tracer, a different set of issues introduce error into its measurement. OCS is present in the atmosphere at a level of a million times less than CO_2 and signal-to-noise detection is challenging. The uncertainty of atmospheric transport modeling makes it difficult to attribute changes in atmospheric signal to changes in surface uptake. Fortunately, we can measure OCS and CO_2 at the same geographic point to remove some uncertainty of atmospheric transport, which affects both gases equally, and help interpret the observations.

114 Many OCS-specific problems incidentally produce useful data. Though not as significant as 115 plant uptake, soils can produce or consume OCS, governed principally by soil temperature and 116 moisture content. The uptake of OCS is light-independent and the ratio at which OCS is taken 117 up relative to CO₂ changes with light levels: at low light, plants can still take up OCS while 118 photosynthesis starts shutting down. This means that OCS draw down is controlled by stomatal 119 conductance regardless of light. Nighttime stomatal conductance is an important parameter for 120 studying the water cycle. OCS observations can give us more information about how much 121 water escapes out of plant stomata during the dark night.

122 Data Serendipity

Now is the right time for getting into measurements of SIF and OCS, thanks to recent technical
innovations. It is notable how much new information we have already extracted with SIF and
OCS with the little data collected. Both SIF and OCS global, long term datasets were generated

126 by instruments that were designed to measure other phenomena. OCS concentrations were 127 included in the NOAA Global Flask Network data on a detector originally configured to quantify 128 other low-concentration atmospheric gases. New commercially available detectors are targeted 129 specifically at OCS, addressing some of the measurement problems that plagued the pioneers of 130 these observations. SIF observations require a high spectral resolution spectrometer to 131 distinguish "additive" fluoresced photons from "reflected" photons in reflected sunlight, and 132 high spatial resolution footprints to distinguish land types. Thankfully, several existing and 133 planned satellites collect such data, but the small signal of SIF is difficult to extract from the 134 noise.

The fluorescence of leaves has been known since the 1870s, but fluorescence observable as distinct from sunlight wasn't demonstrated until 1990. Spectrometers are now available to make this measurement remotely in the air and on the ground; however, some manufacturers do not prioritize consistency between instruments. The observation of SIF requires careful calibration of a spectrometer: most calibrations will lead to a reported concentration of photons that correlates to carbon uptake, but inter-comparison of absolute measurements is important.

Currently, quantum cascade lasers can be configured to measure OCS concentrations frequently enough for ecosystem flux measurements. OCS is present in the atmosphere at a concentration around half a part-per-billion. Before 2010, OCS had to be measured via a complicated preconcentration step before injection into a gas chromatograph with an appropriately sensitive detector. Early studies suffered from high labor cost and method-process mismatches. These initial studies of leaf and soil OCS exchange fueled the desire to try and extract OCS signals out of noisy satellite spectroscopic data. 148 New satellite observations of SIF and OCS provide a more comprehensive look into the regions 149 of the world, such as the tropics, where feedbacks between climate, carbon, radiation, clouds, 150 and water are moderated by photosynthesis. The satellite-based SIF measurements, when paired 151 with other satellite measurements of carbon cycle tracers such as CO₂ and CO, have transformed 152 our understanding of how climate perturbations such as ENSO affect the tropical carbon cycle. 153 The satellite OCS data, when paired with aircraft measurements, provide direct evidence for a 154 substantive tropical oceanic source; updating the OCS budgets is an important step towards using 155 these data to quantify seasonal photosynthesis variability. Current OCS and SIF satellite data 156 over tropical regions is relatively sparse and likely to remain so, underscoring the importance of 157 combining space-based methods with airborne and tower-based measurements to reduce 158 fundamental uncertainties in the processes controlling the carbon cycle.

159 Challenges Remain, but the Future Looks Bright

160 The scientific community would benefit from space-based sensors specifically designed to 161 measure OCS and SIF, coordinated with ground measurements. SIF has had a head start, and 162 two recent articles in Science demonstrate how satellites such as GOSAT and OCO-2 are being 163 used to address remaining challenges. Sun et al., (2017) used the power of OCO-2 SIF to 164 distinguish GPP across land uses and coordinated airborne measurements to validate satellites 165 and capture within pixel variability. Liu et al., (2017) leveraged GOSAT and OCO-2 SIF and 166 CO_2 to break down the tropical carbon cycle into a discrete set of ecosystem processes, which 167 interact with carbon and climate in unique, and previously unknown, ways.

168 Additionally, a new satellite was just launched and two others are planned for SIF measurements.

169 The TROPOMI satellite has already collected nearly two years of data continuously in time

(daily) and space (7x3.5 km²) combining the strengths of approaches used for previous satellite
missions (Köhler et al. 2018). The OCO-3 sensor has been measuring SIF on ISS with other
ecosystem tracers (biomass from GEDI, evapotranspiration from ECOSTRESS) since June 2019.
GeoCarb is targeted for launch in 2022 and will be the first geostationary satellite to measure
SIF.

175 OCS measurements have been retrieved from satellite spectrometers that were already launched, 176 but no OCS-specific space-based sensors are planned for the future. Several satellite products 177 report OCS measurements in the upper troposphere and stratosphere: NASA's TES (Kuai et al. 178 2014), ESA's MIPAS (Glatthor et al. 2017) and IASI (Vincent and Dudhia 2017) and the 179 Canadian Space Agency's recently improved ACE-FTS (Kloss et al. 2019). This latter product 180 can also be used to estimate ratios of OCS isotopologues (Yousefi et al. 2019). For ecosystem 181 science applications, OCS boundary layer measurements are needed to supplement satellite 182 observations, particularly over land. A targeted satellite approach could make OCS estimates 183 nearer to the Earth's surface possible and open up a wider field of questions that OCS data can 184 answer.

Combining both SIF- and OCS-based tools is a very powerful method of measuring global plant activity. This article was conceived at the OCS, CO₂, and SIF study funded by the W.M. Keck Institute for Space Studies in 2017. At the time, we did not have enough data analyzed to harmonize the two approaches and compare estimates of photosynthesis on large scales. This will be the goal of an upcoming workshop in 2021. With a suite of other more established tracers, like heavy water, we can get a better picture of how much carbon is flowing into ecosystems and how much water is escaping back into the atmosphere. When we have a more

192	accurate map of ecosystem function, we can explore and improve our existing process-based
193	ecosystem models. We need to understand how the Earth is breathing now to know how resilient
194	it will be to future change.
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198	Further Reading

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Figure 1 (Diagram). OCS is a gas present everywhere in the troposphere at around 0.5 partsper-billion. OCS is destroyed in plant leaves by the same enzymes as CO₂ and in proportion to how wide the stomata or "front door" of photosynthesis is open. SIF are new photons produced when leaves receive more light than can be used. Some of these photons have wavelengths the sun does not make and can be distinguished from reflected sunlight.



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- **Figure 2 (Photo).** Troy Magney and Katja Grossmann maintain a SIF-enabled spectrometer on a
- tall tower used to measure CO₂ at Niwot Ridge, Colorado. Surface trace gas exchange
- 244 measurements using a combination of techniques allow us to compare traditional to cutting edge
- 245 datasets and benchmark new observations from satellites. Photo courtesy of Christian
- 246 Frankenberg.